Comparative Evaluation of the Microwave-Assisted Extraction in Closed system and Sonication for the Extraction of Polycyclic Aromatic Hydrocarbons from Sediments

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Abstract

The extraction methods for the determination of polycyclic aromatic hydrocarbons (PAHs) from spiked sediment containing benzo[k]fluoranthene, chrysene, acenaphthene, anthracene, carbazole and indeno[1,2,3-c,d]pyrene, using pressurised microwave-assisted (PMAE) and sonication extraction were optimised. Each PAH in the spiked sediment was quantified by using the spectrofluorometric method. The optimised methods were compared on the extraction efficiency of 14 PAHs in a certified sediment reference material, LGC 6188. Recoveries of 14 PAHs were performed by HPLC-DAD at 254 nm using the standard addition method. The results showed that the most efficiency extraction method was PMAE with cyclohexane:acetone (3:2) for 15 min at 140% boiling point of acetone. Under this condition for the extracted certified sediment reference material recovery was 96.55%.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental contaminants possessing high mutagenicity and carcinogenicity (Perez et al., 1998; Pino et al., 2001). The most widely used method for the extraction of PAHs are liquid-solid Soxhlet extraction and sonication technique. (Guerin, 1999; Shu et al., 2000; Song et al., 2002; Brilis and Marsden, 1990). Of the new techniques that have appeared in the last few years, microwave extraction (ME) may provide a good alternative. ME has been used to reduce the volume of solvent required, improve the precision of analyte recoveries, reduce extraction time, minimize the consumption of energy and decrease costs (Tomaniova et al., 1998).

The aim of the present study was to compare the optimum extraction efficiencies of PAHs by the recently introduced PMAE with the efficiencies obtained by conventional sonication extraction.

This work also discusses the use of closed-vessel microwave-assisted extraction to recover PAHs from sediments. Solvent type and the time and temperature of irradiation were varied systematically to determine the optimum conditions for the extraction of PAHs from spiked sediment samples.

Materials and Methods

Chemical: All reagents used were of analytical reagent grade. Solvents for HPLC were of that grade. A mixture of components PAHs, each 10 ng μl^{-1} in acetonitrile was purchased from Sigma-Aldrich. A certified reference material, LGC 6188 was purchased from Laboratory of the Government Chemistry, UK. Spiked sediment sample: A solution consisting of benzo[*k*]fluoranthene, chrysene, acenaphthene, anthracene, carbazole and indeno[1,2,3-*c,d*]pyrene was spiked into a dried sediment from the Mekong River.

Apparatus: The Mars-X (CEM Corporation, USA) PMAE and CREST Ultrasonic bath (Crest ultrasonic cooperation) were used for the extractions. The Cary Eclipse spectrofluorometer (Varian, USA) was used to analyse each PAH in the sample. The HPLC system was composed of an Agilent 1100 series binary pump system, a 1100 DAD and a ChromSpher PAHs:250 X 4.6 mm I.D. (Varian, USA) column.

Extraction procedure:

-Microwave-assisted extraction procedure

All extractions were carried out in triplicate. A 0.25 gram of the spiked sediment sample was placed in the lined extraction vessel, covered by 20 ml of solvent and placed in the MARS-X. microwave extraction system. The type of solvent and the time and temperature of irradiation were varied systematically. The extraction solvents used were methanol, acetonitrile, acetone, dichloromethane, hexane:acetone (3:2) and cyclohexane:acetone (3:2). The times of irradiation were varied from 3 to 20 min and the temperatures of irradiation were varied from 60% to 120% of the boiling point for each exctraction solvent.

-Sonication extraction procedure

The extraction was carried out in closed system and triplicate for each extraction condition. A 0.25 gram of the spiked sediment sample was placed in a glass vessel for sample preparation, covered by 20 ml of extraction solvent and placed to the ultrasonic bath. The type of extraction solvent and time of irradiation were varied in this work (temperature of extraction was measured for each extraction process). The extraction solvents used were the same as in the microwave-assisted extraction procedure. The times of irradiation were varied from 10 to 50 minutes.

-Recovery

The certified reference material, LGC6188 was used for the recovery study. 0.25 gram of LGC 6188 was weighed accurately for determining the recovery of each optimum extraction method. Analyses of 14 PAHs from in the extracts were performed by HPLC using the standard addition method. Each extraction was carried out in triplicate.

Results and Discussion

Optimization of microwave condition:

A spiked sediment sample was selected in order to test the influence of different parameters (type of solvent, time of irradiation and temperature of irradiation) on the total amount of PAHs extracted in mg/g of sediment.

-The influence of extraction solvent

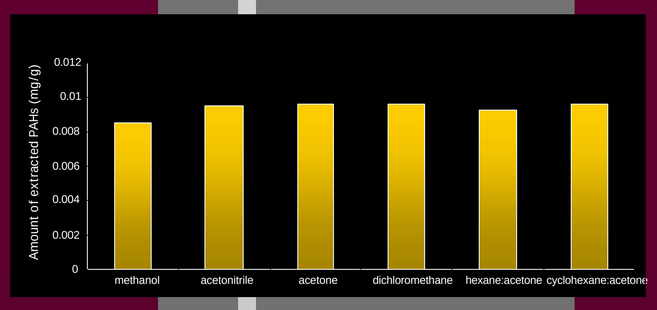

Figure 1 Total amount of extracted PAHs obtained by PMAE with various solvent

-The influence of extraction time

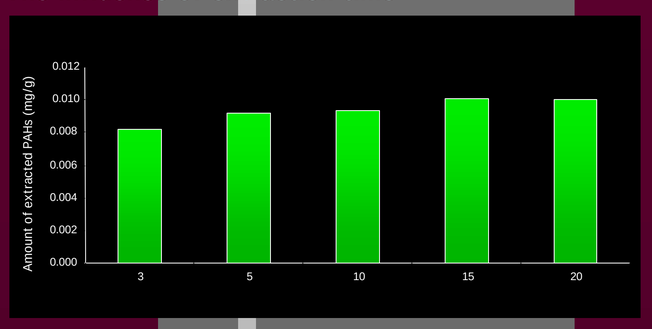

Figure 2 Total amount of extracted PAHs obtained by PMAE as a function of time using cyclohexane:acetone (3:2)

-The influence of extraction temperature

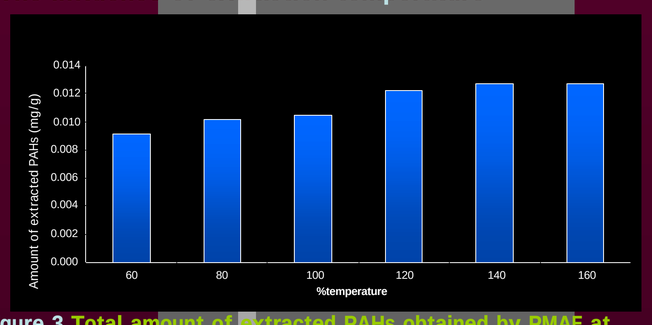

Figure 3 Total amount of extracted PAHs obtained by PMAE at various temperature using cyclohexane:acetone (3:2)

The optimized conditions for extracting PAHs from sediments by pressurized microwave-assisted extraction have been optimized. The optimization of all parameters (types of extraction solvents, times of irradiation and temperatures of irradiation) were important for efficient extraction. From the result, the efficient microwave extraction conditions was obtained with 20 ml of cyclohexane:acetone (3:2) for 15 minutes at 140% boiling point of acetone (79.0 °C). The optimal conditions were used for the extraction of certified reference material (LGC 6188) for recovery testing.

Optimization of ultrasonic extraction condition:

A spiked sediment sample was selected in order to test the influence of different parameters on the total amount of PAHs extracted in mg/g of sediment.

-The influence of extraction solvent

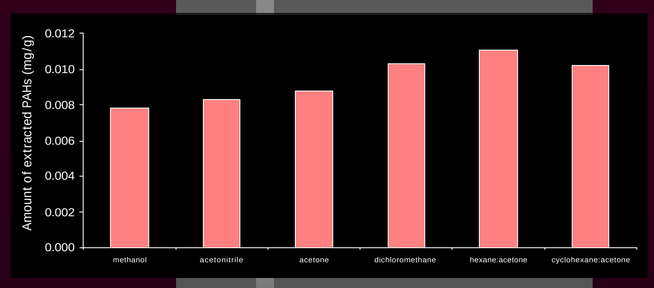

Figure 4 Total amount of extracted PAHs obtained by sonication with various solvent

-The influence of extraction time

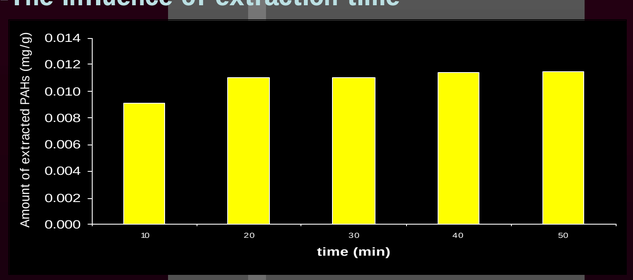

Figure 5 Total amount of extracted PAHs obtained by sonication as a function of extraction time

The conditions for extraction of PAHs from sediments by ultrasonic extraction have been optimized. The types of extraction solvents and extraction time were important in order to receive the good extraction efficiency. The results from the previous sections showed that the optimal condition was obtained with 20 ml of hexane:acetone (3:2) for 40 minutes. This condition was used for the extraction of certified reference material (LGC 6188) for recovery testing.

Recovery of the PAHs in optimized extraction methods using certified reference material

To compare the %recovery of each extraction method, The PAHs in certified reference material (LGC 6188) were extracted using the optimized conditions of each extraction method: microwave extraction with with 20 ml of cyclohexane:acetone (3:2) mixture at 140% of boiling point of acetone for 15 minutes; ultrasonic extraction with 20 ml of hexane:acetone (3:2) mixture for 40 minutes. The extracted PAHs were analyzed by HPLC using the standard addition method under the condition of EPA 8310 method. The amount of extracted PAHs was expressed in term of mg/kg of sediment as the individual PAHs. The analytical results from each extraction was compared as shown in the Table 1 and Figure 6.

Table 1 Amount of extracted PAHs in certified reference material of each extraction method by optimized condition

PAHs	Certified value, uncertainty (mg/kg)	PMAE (mg/kg)	Sonication (mg/kg)
acenaphthene	0.070, 0.02	0.053±0.71	0.013±10.12
fluorene	0.120, 0.04	0.129±11.01	0.047±3.85
phenanthrene	1.040, 0.30	0.987±4.99	0.720±14.94
anthracene	0.360, 0.11	0.407±2.50	0.281±5.34
fluoranthene	1.790, 0.35	1.354±1.30	1.047±2.26
pyrene	1.480, 0.50	1.397±0.67	0.807±0.81
benzo(a)anthracene	0.830, 0.18	0.741±1.17	0.276±5.86
chrysene	0.830, 0.16	0.855±2.01	0.742±3.62
benzo(b)fluoranthene	0.820, 0.19	1.018±5.91	0.922±0.30
benzo(k)fluoranthene	0.500, 0.35	0.884±1.55	0.820±0.98
benzo(a)pyrene	0.650, 0.14	0.596±0.21	0.291±8.36
dibenzo(a,h)anthracene	0.130, 0.05	0.102±2.69	0.069±1.01
benzo(g,h,i)perylene	0.360, 0.13	0.396±3.39	0.296±3.10
indeno(1,2,3,cd)pyrene	0.370, 0.14	0.325±1.50	0.227±3.56

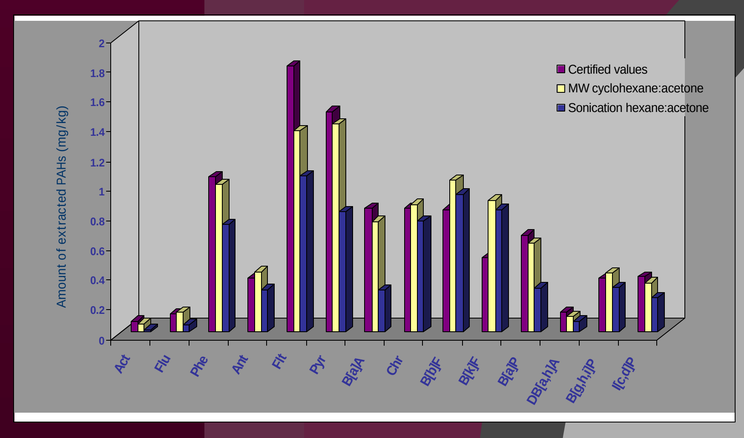

Figure 6 Amount of individual extracted PAHs in certified reference material of each extraction method by optimized condition

The results indicated that the microwave extraction using 20 ml of cyclohexane:acetone (3:2) mixture at 140% of boiling point of acetone for 15 minutes gave highest extraction efficiency. When compared to the certified value, the total %recovery obtained by microwave extraction was 96.55%. The reproducibility was also satisfactory (%RSD less than 0.76% for the total amount of extracted PAHs). The individual %recovery were approximately 75%, for only a few PAHs such as acenaphthene, fluoranthene and dibenzo[a,h]anthracene and the others were close to 100%.

Conclusion

The experimental results indicated that the PMAE was a good alternative to extract PAHs in sediment and soil comparing to sonication method. Its main advantages are the reduction of the volume of volatile organic solvent, the reduction in extraction time and lower consumption of energy.

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Acknowledgement

The authors gratefully acknowledge the Postgraduate Education and Research Program in Chemistry (PERCH) and Kasetsart University Research and Development Institute (KURDI) for the financial support. We wish to express our gratitude to the Department of Chemistry, Kasetsart University, for all the facilities provided for this research program. We are also grateful to the central laboratory of Faculty of Science, Kasetsart University, for the access to the spectrofluorometer. Finally, we would like to thank Dr. A.F. Gaines, University of Strathclyde, U.K., for his valuable comments and suggestion.